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Stereochemistry of heterocycles - XVIII. Configurations and preferred conformations of some 4,5-dialkyl-5-methoxymethyl-and 2,2,4-trimethyl-5-alk-l-5-methoxymethyl-1,3-dioxanes

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Abstract

A group of previously undescribed methoxymethylalkylacetoacetic esters were obtained by the reaction of monochloromethyl ether with sodium salts of alkylacetoacetic esters. The reduction of the new esters with lithium aluminum hydride gave 2-alkyl-2-methoxymethyl-butan--1,3-diols. In connection with the fact that the reduction is stereochemically regulated by the rule of asymmetric induction, the erythro isomers predominate in stereoiso-meric mixtures of the 1, 3-diols. 4,5-Dialkyl-5-methoxymethyl- and 2,2,4-trimethyl-5-alkyl-5-methoxymeth-l-1,3-dioxanes (mixtures of the stereoisomers with predominance of the trans isomers) were synthesized by the condensation of 2-alkyl-2-methoxymethylbutane-1,3-diols with formaldehyde and acetone. The stereoisomers were separated by precision rectification, and their configurations and preferred conformations were proved by PMR and IR spectroscopy. The low-boiling isomers of the 1,3-dioxanes under discussion are the trans isomers, while the high-boiling isomers are the cis isomers; the preferred conformation for these isomers is a somewhat distorted chair.

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